IMPROVEMENT OF THE USEFULNESS OF PYROLYTIC GRAPHITE IN ROCKET MOTOR APPLICATIONS (U)

Contract No. DA-36-034-ORD-3279 RD

Project No. TB4-004

Quarterly Progress Report

December 1961 through February 1962

91000

ATLANTIC RESEARCH CORPORATION

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March 20, 1962

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March 15, 1962

Commanding General
Army Ordnance Missile Command
Redstone Arsenal, Alabama

Attention: ORDXM-RKX

Gentlemen:

Attached you will find a Quarterly Progress Report on Contract No. DA-36-034-ORD-3279RD, entitled "Improvement of the Usefulness of Pyrolytic Graphite in Rocket Motor Applications." This report covers the period from December 1, 1962 through February 28, 1962.

Very truly yours,

ATLANTIC RESEARCH CORPORATION

James D. Batchelor

James D. Batchelor
Project Director

JDB:clr

Encl.

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I. INTRODUCTION AND SUMMARY

This report covers the work performed during the quarter starting December 1, 1961 and ending February 28, 1962. Research and evaluation on deposition process conditions and the evaluation of pyrolytic graphite coatings in sub-scale rocket motor nozzle tests continued. The deposition studies emphasized means of improving the fabrication of pyrolytic coatings of useful quality. The motor tests of coated nozzles were designed to measure the inherent serviceability of pyrolytic graphite under severe conditions using an advanced propellant of 6500°F flame temperature. In line with the interest of the sponsor (Ordnance Material Research Office) the principal goal of this program continues to be the definition, in detail, of the serviceability of good quality pyrolytic graphite coatings under a variety of severe nozzle environmental conditions selected to cover the range found in missile development programs.

Deposition runs, in which pyrolytic graphite was formed at a low temperature (1340°C) on tubular substrates of three different grades, showed significant differences in the microstructure of the coating. The deposit on a relatively non-graphitic substrate had a finer microstructure than that on the standard graphite substrate. The coating on a high-purity, coarse-grained graphite had a coarser structure. Steam pretreatment of the substrate produced an increase in the cone size in pyrolytic graphite which was probably caused by increased activity of local sites on the substrate surface.

Pyrolytic graphite nozzles were tested in three rocket motor firings to define the effect of motor pressure on the erosion rate of the standard (2000°C) coating. A fourth motor test indicated that a lower temperature coating (1700°C) was not serviceable with the 6500°F propellant. Further motor tests are planned to determine the serviceability of pyrolytic graphite under various motor operating conditions.

II. DEPOSITION-PROCESS STUDIES

The relationship of the deposition-process variables to the quality of the pyrolytic graphite coating is not being approached as an optimization program but rather as a search for methods to simplify conditions or use less expensive equipment. A good grade of pyrolytic graphite currently produced at 2000°C permits evaluation in rocket nozzle tests to proceed independent of the deposition studies.

As outlined in the last quarterly report, the effect of surface condition of the substrate on the microstructure of the coating is being studied. Lower deposition temperatures are also being evaluated. Accordingly, two series of deposition tests were made. In the first, the effect of the graphitic nature of the substrate and its purity were observed. Pyrolytic graphite was deposited on three different substrates at 1340°C. Deposition conditions are given in Table I. Photomicrographs of the polished cross-section of each coating are shown in Figure 1. The substrate in Run 42 was grade AGOT (National Carbon Co.) which is a high-purity graphite produced for nuclear applications. In Run 43, the substrate was the standard grade of graphite pipe used in most of the studies to date. The substrate for Run 44, taken from another lot of the graphite pipe, was chosen because of the markedly less graphitization of this batch (as measured by X-ray diffraction patterns) compared to the normal graphite pipe.

The coating formed on each of these substrates was rather coarse, which is characteristic of the low-temperature (1340°C) deposit. However, the deposit on the less-graphitic substrate was somewhat finer-grained and was of a more uniform microstructure than that formed on the standard graphite substrate. The pyrolytic deposit on the AGOT graphite was coarser and rougher than that on the standard substrate, but this coarseness was probably caused, at least in part, by the coarse surface of the AGOT material.

To obtain further data on the effect of surface condition on the coating microstructure, a second series of tests was carried out with a steam activation pretreatment of the substrate. For Run 45, a graphite substrate was exposed to argon saturated with

TABLE I. Deposition Conditions

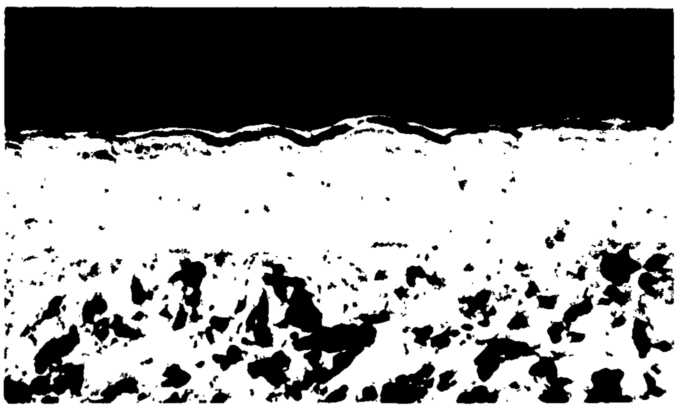
Run No.[a]	Substrate Temperature (°C)	Substrate Material	Substrate Pretreatment	Carbon-Source Gas	Source Gas Concentration (per cent)
42	1340	AGOT Graphite	None	Propane	2.5
43	1340	Graphite[b] Pipe, Lot 1	None	Propane	2.5
44	1340	Graphite[b] Pipe, Lot 2	None	Propane	2.5
45	2000	Graphite[b] Pipe, Lot 1	Water-saturated Argon, 15 min. at 2000°C	Methane	5.0
46	2000	Graphite[b] Pipe, Lot 1	None	Methane	5.0

[a] Conditions common to each run
1. Ten per cent of gas flow entered outside of injector
2. Total gas flow of 20 SCFH
3. Substrate surface finish, 80 grit

[b] Of the two graphite pipe lots, Lot 1 showed a much more graphitic X-ray diffraction pattern than did Lot 2 which resembled baked carbon.

Run 42 X150

Run 43 X150



Run 44 X150

Figure 1. Microstructure of Deposits on Different Substrates at 1340°C

water vapor at room temperature for 15 minutes immediately prior to deposition. The pretreatment and the deposition were both carried out at 2000°C. Run 46 was a control test in which all conditions were the same as Run 45 except that the steam pretreatment was eliminated. The deposit on the steam-pretreated substrate had an increased cone size, especially near the surface. Typical areas are shown in Figure 2. This increased cone size was probably caused by an increased activity of a number of reactive sites at which rapid nucleation and growth occurred. This is consistent with the activation process which would occur through steam treatment.

The results from both of these series of tests suggest that a uniform microstructure of reduced cone size requires a surface on the substrate which is moderately smooth and as uniformly inactive (chemically) as possible. Further trials are planned to test this postulate. During the coming quarter, a special effort will be made to determine the improvement which can be achieved through substrate surface preparation. In this way, the final six months of the program can be used to test nozzles prepared by the most promising deposition techniques. This amount of lead time will allow definitive nozzle tests of any special grades of pyrolytic graphite.

Run 45 X150

Run 46 X150

Figure 2. Effect of Steam Pretreatment on Microstructure of Pyrolytic Graphite

III. MECHANICAL DESIGN STUDIES

Analytical studies of the stress-strain relationships for pyrolytic graphite coatings on graphite substrates have been summarized in previous reports on this contract. Difficulties were encountered in completely defining the shear stresses which exist at or near the edge of a coated section of a normal nozzle contour. Consideration of this problem during the current quarter indicated that the gain to be realized in pursuing this mathematical analysis further is no longer consistent with the program goals requested by the sponsoring agency. Thus, no further detailed analysis was carried out during the current period.

The advantages of a nozzle made of several individual coated segments stacked together appear worthwhile based on a qualitative study of the stress relation. It appears that segments of relatively short length will prove more serviceable than longer nozzle sections. Short segments reduce the curvature of each section and may reduce the magnitude of the stresses at the edges. Nozzle test results from other programs may allow a check to be made of this proposition. The nozzles tested in this program use a segmented design principally because of the ease of fabrication and characterization of such test pieces. However, the success of these pieces may be the result of improved stress distribution in the segmented design.

IV. MOTOR FIRING TESTS

As discussed in the previous quarterly report, pyrolytic graphite withstands the 5600°F flame temperature of an aluminized Arcite propellant so well that little differentiation between test nozzles is possible. Thus, the motor firings this quarter were all made using an aluminized Arcocel propellant with a 6500°F flame temperature. Some further tests with the 5600°F propellant, especially of pyrolytic graphite coatings formed at lower temperatures, will be necessary as the program progresses.

Two motor tests were made this quarter using one-piece, fully coated nozzles because an early test indicated the three-piece, segmented test nozzle might be unsuitable. The indication was that erosion of the best molded graphite entrance section of the segmented nozzle was quite noticeable in every test with the 6500°F propellant. It has been concluded, however, that this problem is not critical and that the segmented nozzle can be used satisfactorily for our test program. Since the segmented nozzle is easier to fabricate and easier to examine, before and after a firing, the two other motor tests completed this quarter used the segmented nozzle design. Figure 3 shows a three-piece, segmented nozzle before final assembly.

Six furnace runs were made for nozzle preparation. In four of these, pyrolytic graphite was deposited on contoured sections of segmented nozzle pieces. One-piece nozzles were coated in the other two runs. All of the runs except one were made at 2000°C to produce the standard grade pyrolytic graphite coating. In the remaining run, a contoured section was coated at a substrate temperature of 1700°C. Complete data are shown in Table II.

Four nozzle test pieces were tested with Arcocel 163 (6500°F) propellant. A summary of the data is shown in Table III. The first three firings used the standard 2000°C pyrolytic graphite coating. In the first test, PYB-3, a segmented nozzle performed extremely well at low motor pressure (350 psi). Erosion was negligible. Comparison of the behavior

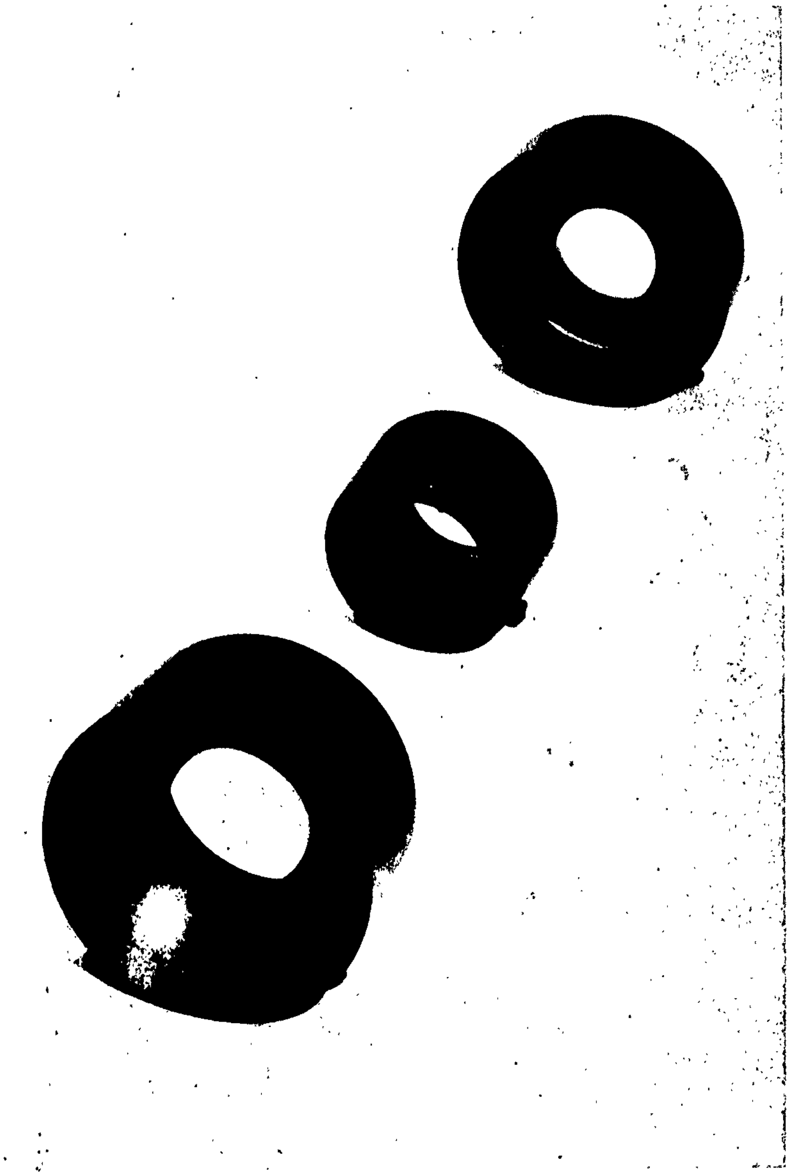


Figure 3. Segmented Test Nozzle Before Assembly for Test with 6500°F Propellant.

TABLE II. Nozzle Fabrication Runs

Run No.	Substrate Temperature (°C)	Total[a] Gas Flow (SCFH)	Run Duration (hr)	Substrate Geometry	Substrate Throat Diameter (inch)	Coated Throat Diameter (inch)
N-7	2000	10	2.5	Full nozzle	0.590	0.519/.523
N-8	2000	10	2.2	Full nozzle	0.590	0.527/.530
N-9	2000	8	2.0	Contoured throat section	0.580	0.552
N-10	1700	10	2.0	Contoured throat section	0.580	0.517 (finished to 0.520)
N-11	2000	8	2.25	Contoured throat section	0.580	0.552
N-12	2000	8	3.66	Contoured throat section	0.580	0.539

[a] Gas flow consisted of 5 per cent methane in argon. Ten per cent of argon introduced outside of injector.

TABLE III. Motor Test Firings with Arcocel 163 (6500°F) Propellant

Firing No.	Fabrication Run	Average Motor Pressure (psi)	Firing Duration (sec)	Nozzle Diameter (inch)		Average Erosion Rate (mil/sec)
				Before	After	
PYB-3	N-6	350	35.5	0.558	0.556/.559	0.0
PYB-4	N-7	468	66.2	0.519/.523	0.594/.620	0.65 0.52 (based on coating)
PYB-5	N-8	600-750 (est.)[a]	46(est)[a]	0.527/.530	0.561/.648	0.36 (at min. dia. point)[b]
PYB-6	N-10	322	68.3	0.520	0.670/.712	Coating removed completely

[a] Estimated from ballistic properties because of instrumentation failure.

[b] Calculated away from gouge in nozzle produced by back-up failure.

of this nozzle at low motor pressure with that reported last quarter for PYB-2 fired at high motor pressure (830 psi) indicated clearly the extreme importance of motor pressure in defining the serviceability of pyrolytic graphite coatings. Figure 4 graphically represents this effect of motor pressure on erosion rate.

The other two tests of the standard 2000°C coating with Arcocel 163 (6500°F) propellant, also included on Figure 4, require some further discussion because of difficulties encountered with these nozzles. Both of these tests, PYB-4 and PYB-5, were made with fully coated, one-piece nozzles. These one-piece nozzles were prepared as a hedge against the problem of failure in the molded graphite entrance section of the segmented nozzles. In test PYB-4, the pyrolytic graphite coating was eroded through in the 66.2 second firing duration. The average erosion rate of 0.65 mil/sec was naturally greater than that to be expected from the coating alone because of the rapid erosion of the unprotected substrate toward the end of firing. However, even the erosion rate of 0.52 mil/sec based on removing just the coating appears higher than anticipated for the moderate average pressure in the motor chamber during this test (468 psi). Thus, the quality of this coating remains suspect with the probability that some spalling, rather than uniform erosion, of the coating occurred during firing. The erosion rate for this test thus lies above the line in Figure 4 which represents coatings of good performance. During firing PYB-5, the backing material failed locally and produced a gouge in the nozzle which introduced considerable uncertainty in the calculated erosion rate. Assuming that the minor diameter of the fired nozzle (approximately 90° from the gouged area) represents the basic erosion pattern for this test, an erosion rate of 0.36 mil/sec was calculated. The average chamber pressure during test also is uncertain because of an instrumentation failure. The average was calculated from ballistic considerations with the uncertainty shown in Figure 4 by the horizontal line through this data point. The uncertainty in the results from these two full-nozzle tests is unfortunate and further tests are planned to better define the effect of motor pressure on erosion rate.

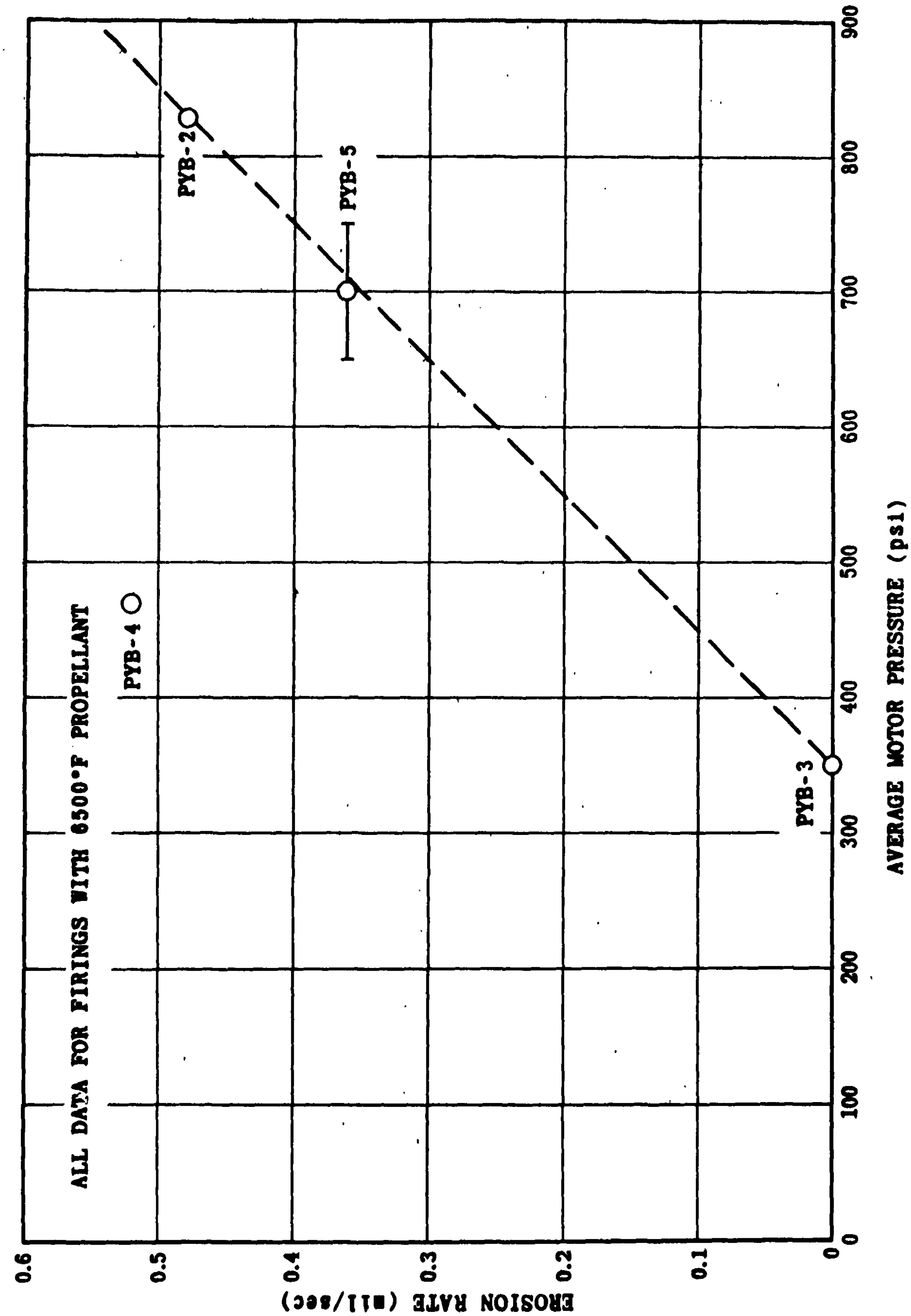


Figure 4. EFFECT OF MOTOR PRESSURE ON NOZZLE EROSION RATE FOR 2000°C PYROLYTIC GRAPHITE.

The final motor test of this period used the segmented nozzle prepared with a 1700°C-pyrolytic graphite coating. This coating was completely eroded away during the 68-second firing. Although the surface of this coating was coarse, as deposited, and was polished smooth before the test, the indication is that coatings made at lower deposition temperatures may not be serviceable with 6500°F propellant. Some motor tests will be scheduled with coatings produced at lower temperatures using Arcite 373 (5600°F) propellant for screening purposes before further tests are made with such coatings in the hotter propellant.

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